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13. ABSTRACT (Maximum 200 words)

Research has been performed using high resolution electron microscopy under ultra-high vacuum (UHV) conditions on a number of metal-semiconductor systems. A new system combining classical surface characterization techniques and growth has been installed on a UHV microscope and fully tested. The growth at the monolayer level of Au and Ag on Si (001) has been studies combining XPS and electron microscopy. Studies of the growth of Au on both air introduced and Ga-rich GaAs (001) substrates have been performed. A variety of new methodologies and techniques have been developed, most notably atomic scale imaging of surfaces at a higher level than previously possible and new methods of determining surface structures just from electron (or x-ray) diffraction data. Electron microscopy studies of MoS_2 lubricant films are also described.

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FINAL TECHNICAL REPORT

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Introduction

The primary focus of the work was to look at the initial stage nucleation and growth of metals on semiconductor surfaces, typical thicknesses of 1-5 nm, with a view towards improving the understanding of ohmic metal contacts. In order to perform these studies a new surface science multichamber system was attached to an existing transmission electron microscope. Experiments were performed for gold and silver on Si (111) and Si (001) surfaces as well as gold on GaAs (001) surfaces. Additional collaborative work on MoS_2 films was also performed. The main conclusions of this work are summarized below.

SPEAR

A major component of the effort involved installing, testing and bringing to full operation a multichamber surface science system called "SPEAR". The design target of the SPEAR system was to couple conventional surface science characterization techniques such as XPS and Auger with both growth and electron microscopy characterization, all with the sample(s) never leaving a UHV environment. While the hardware for this system was supported from a separate grant (NSF-DMR), putting the various pieces together was not. After approximately four (graduate student) man years of effort this was achieved without compromising the high resolution performance of the UHV transmission electron microscope to which it was attached in any way. We were able to demonstrate full exploitation of standard surface chemical characterization of small electron microscope samples, as well as ready sample transfer [8]. To put this a

little in perspective, with the original system only one sample could be used at a time, typically for a period of one month; we now simultaneously handle about a dozen samples and sample preparation times have been reduced from weeks to days. The system is now fully functional and being exploited for systematic growth studies particularly of hard coatings, both as part of a continuation AFOSR grant (focusing on cubic BN) and via an NSF-MRSEC grant (magnetron sputtering and ion beam deposition of various hard coatings). In many respects it represents the first of a new class of UHV electron microscopes where the microscope itself is only a relatively small component of a much larger system; at the time of writing at least three larger systems are being constructed in Japan using a similar approach.

Nucleation and Growth of Metal on Semiconductor Surfaces

We have worked rather extensively on the nucleation and growth of metals on semiconductors. The work splits into two areas, namely work on silicon and work on gallium arsenide.

Metal on Silicon

The gold on silicon (111) system [4,5,11,14] (ASSERT grant F49620-92-J-0250) and gold [6,12] or silver [7] on silicon (001) have both been studied. For the former, we have been able to complete the phase diagram below one monolayer [13] including determination of all the relevant structures [4,5]. For the silicon (001) substrates we were able to obtain the first atomic structure model of the Au 5x3 surface [6], determine an unusual growth mode for Ag [7] and study in detail the growth of Au on silicon (001) at room temperature [12]. In the later we were able to refute a commonly accepted belief that some form of silicide was formed, the evidence for this being changes in the gold XPS and Auger. Using the SPEAR system [8] we were able to obtain images and (XPS and Auger) spectra of the same sample, demonstrating that the growth was not layer-by-layer as had been thought in the past. This general line of research extended to Stranski-Krastanov growth in binary eutectic systems is continuing under separate funding.

Metal on GaAs

We have studied the growth of gold on air exposed GaAs (001) surfaces as well as Ga rich surfaces produced by ion bombardment. The initial results are summarized in the Ph.D. thesis of Dr. G. Jayaram and are:

1) The initial structure at room temperature on a contamination free (Ga rich) surface is polycrystalline in nature. Above a critical thickness value the Au appears to react as evidenced by XPS peak splitting.

2) On annealing epitaxial Au or $AuGa_2$ is formed with the epitaxial relationships:

$AuGa_2$; Au (001) // GaAs (001) and <110> // GaAs <110>

3) The presence of carbon or oxygen at the surface prevents alloy formation and prevents reaction with the GaAs substrate.

After installation of the SPEAR system, further experiments were performed to try and produce As terminated surfaces by annealing in an As atmosphere. A number of experiments were performed, leading to the conclusion that the as supplied indirect heating method gave too high a thermal gradient across the samples, and an alternative heating strategy would be required for good thermal control. In the end, rather than purchasing (for instance) an infra-red heating source and in light of an impending conversion of the initial MBE chamber to one for the growth of cubic BN, no further experiments were performed.

Technique and Methodology Development

Throughout the grant we have been involved with developing techniques and methods for improving both sample preparation as well as our ability to obtain information. Two particular "targets of opportunity" are described below, but in addition to these:

1) We have developed reliable methods of preparing electron transparent clean substrates of essentially any material [3]. This involves controlled ion-beam sputter cleaning at comparatively low energies and careful control of annealing temperatures. The later is particularly critical since it is only within a narrow temperature window that surface diffusion leads to a flat surface without coarsening (via bulk diffusion).

2) We have developed robust methods for quantifying microscope data [2], particularly electron diffraction data, to a level where structure refinement to accuracies of 1pm is relatively straightforward.

New Methods of Surface Structure Determination

Partially supported by a separate ASSERT grant (F49620-92-J-0250), two targets of opportunity presented themselves. The first arose when the student on the ASSERT grant (Richard Plass) was working as an intern for a period of two months at NEC in Japan. The purpose of this was in part to use a different, lower voltage electron microscope to try and obtain improved surface images at a lower voltage. Whereas his experiments were completely unsuccessful, he found a few old images of the Si (111) 7x7 surface taken a few years earlier which, at that time, they were not able to do anything with. After transferring these in digital form to Northwestern we were able to remove noise and separate out independent images of the surface which showed not just the top layers visible by scanning tunneling microscopy by all the important atoms including the dimers in the third layer. Apart from appearing in Physical Review Letters [10] and some other locations[1], this work has stimulated continued collaborations with both the group at NEC and another group of Japanese scientists at the National Research Institute of Metals in Tsukuba Japan to continue these developments.

The second came about as a consequence of some discussions with Dr. D. Dorset of the Hauptman-Woodman Medical Institute in Buffalo. We supplied him with diffraction intensities from a surface and using these and nothing else he was able to solve the structure using direct methods [13]. (Direct Methods are a fairly routine technique for solving bulk structures using x-ray diffraction, e.g. proteins containing thousands of atoms, but it was thought that they could not be used for surfaces.) This is a significant development since it implies that surface structure determination should become almost a trivial problem within a few years. This has spawned a substantial

[1] Frackfurter Allgemeine Zeitung, January 8th, 1997; Advanced Materials and Processing, June 1997; ARITHMEUM exhibit at Forschungsinstitut for Diskrete Mathematik, Bonn, autumn 1997 onwards

independent and international collaboration primarily involving Dr. C. Gilmore from the University of Glasgow and Dr. R. Feidenhans'l from Risoe National Labs in Denmark.

MoS_2 Thin Films

Throughout the grant period we have been involved in some collaborative work with Dr. M. Hilton from the Aerospace Corporation looking at MoS_2 solid lubricant films [1, 9, 15]. This involved the use of our electron microscopes either for in-situ studies [1] or just as high resolution instruments [1,9]. The first set of experiments [1] involved the use of oxygen to simulate accelerated stability tests. The second a set of "multilayer" metal/MoS_2 films (developed by Ovonics, current licensed to and sold by TA&T Inc.) which in fact were not at all multilayer films, but instead had metal island structures particularly at the lower metal (layer) thicknesses. The final set of experiments [15] characterized cosputtered films (produced by Hohman plating), showing that the most effective films (Sb doped) are morphologically dense with no initial long range order. For reference, both the multilayer and cosputtered films prevent the formation of a columnar structure which improves performance.

Personnel Supported:

G. Jayaram, Ph.D. Thesis entitled "Ultrahigh Vacuum Transmission Electron Microscopy Studies of Semiconductor Surfaces", December 1995, Northwestern University.

R. Plass, Ph.D. Thesis entitled "Gold Induced Si (111) Surface Reconstructions Studied by Ultrahigh Vacuum Transmission Electron Microscopy, June 1996, Northwestern University (Assert Grant F49620-92-J-0250).

C. Collazo, Ph.D. Student

E. Landree, Ph.D. Student

Refereed Publications

1. Ultra High Vacuum High Resolution Transmission Electron Microscopy of Sputter Deposited MoS_2 Thin Films

   Surface & Coatings Technology 68/69, 439 (1994)

   G. Jayaram, N. Doraiswamy, L. D. Marks and H. R. Hilton

2. A Cross-Correlation Method for Intensity Measurement of Transmission Electron Patterns

   Ultramicroscopy 53, 15 (1994)

   P. Xu, G. Jayaram and L. D. Marks

3. UHV-HREM and Diffraction of Surfaces

   Interface Science 2, 381 (1995)

   G. Jayaram, R. Plass and L. D. Marks

4. Atomic Structure of Si(111)-(5x2) Au from HREM, χ^2 Electron Diffraction and Heavy Atom Holography

   Phys. Rev. Letts. 75, 2172 (1995)

   L. D. Marks and R. Plass

5. UHV Transmission Electron Microscopy Structure Determination of the Si (111) √3x√3 R30 Au Surface.

   Surf. Sci. 342, 233 (1995)

   R. Plass and L. D. Marks

6. Atomic Structure of the Si(100)-5x3 Au Surface

   Surface Reviews and Letters, 6, 731 (1995)

   G. Jayaram and L. D. Marks

7. Unusual island structures in Ag growth on Si(100)-2x1

   Physical Review B51, 10167 (1995)

   N. Doraiswamy G. Jayaram and L. D. Marks.

8. Design and Initial performance of an ultrahigh vacuum Sample Preparation, Evaluation, Analysis and Reaction (SPEAR) system.

   C. Collazo-Davila, E. Landree, D. Grozea, G. Jayaram, R. Plass, P. C. Stair and L. D. Marks

   Journal of the Microscopy Society of America 1, 267 (1995)

9. Nanostructure of Au-20% Pd Layers in MoS_2 Multilayer Solid Lubricant Films
G. Jayaram, L. D. Marks and M. R. Hilton
Surface and Coatings Technology,76, 393 (1995).

10. Imaging the Dimers in Si (111) 7x7
E. Bengu, R. Plass, L.D. Marks, T. Ishimiya, P. M. Ajayan, and S. Iijima
Phys. Rev. Letts. 77, 20 (1996).

11. Room temperature deposition of gold onto the diffuse and sharp diffraction spot Si(111) $\sqrt{3}$x$\sqrt{3}$ R30 Au surfaces.
R. Plass and L. D. Marks
Surf. Sci. 357-358, 42 (1996).

12. UHV-HREM and Chemical Analysis of Room Temperature Au Deposition on Si (001)-2x1
E. Landree, D. Grozea, C. Callazo-Davila and L. D. Marks
Phys. Rev. B55, 7910 (1997).

13. Imaging Surface Structures by Direct Phasing
L. D. Marks, R. Plass and D. L. Dorset
Surface Reviews and Letters 4, 1 (1997).

14. Submonolayer Au on Si (111) Phase Diagram
R. Plass and L. D. Marks
Surface Science 380, 497 (1997).

15. Microstructure of Sputter-Deposited Metal- and Oxide-MoS_2 Solid Lubricant Thin Films
M. R. Hilton, G. Jayaram and L. D. Marks
J. Mater. Research, in press